are because of the lack of symmetry of Sharma-Joshi (1963) scheme The transverse branches for DAF model coincides with that for CGW model, suggesting insignificant rotational symmetry of the gold lattice The longitudinal branches show difference at the zone boundary for the two models

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Infrared and Raman spectra of 4-fluro-2-chlorotoluene molecule

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A complete vibrational spectra of toluene, mono-, di- and trihalogenated tohuenes have been reported by many earlier workers In general they have taken the similar atoms for substitutions in the benzene ring and have discussed the effects of these substitutions on the change in the vibrational frequencies Now it has been undertaken to observe the changes in the vibrational frequencies when the substituents are different atoms or a group of atoms at the different positions of the benzene ring. Recently Joshi & Sharma (1974) have reported the infrared spectrum of 2-fluoro-4-chlorotoluene and have reported the changes occuring in the vibrational frequencies Here in the present communication the vibrational spectrum of 4-fluoro-2-colorotoluene molecule has been taken into account and the changes in the frequencies due to the change in the positions in the benzene ring is observed and discussed. Further the observed vibrational data have been used to calculate the thermodynamic functions for 4-fluoro-2-chlorotoluene and 2-fluoro-4-chlorotoluenes under usual approximations *i e.* ideal vapour at one atmosphere assuming the harmonic oscillator and rigid rotator approximations.

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Table 1 Vibrational assignments and comparative study of the fundamentals of 2-fluoro-4-chloro- and 4-fluoro-2-chlorotoluenes

2-Fluoro-4-Chlorotoluene	4-Fluoro-2-Chlorotoluene		Assignments
	Infrared	Raman	
305(11)		305(m)	C-CH_3 o p bending
370(23)		380(w)	C-Cl i p bending
	409(30)	420(s)	C-C-C o.p. bending
443(35)	442(35)		C-C-C o p bending
460(11)	459(39)	465(vs)	C-F o p bending
575(45)	557(32)	575(w)	C-CH_3 i p. bending
	683(36)	686(vs)	C-C-C o p bdnding
752(22)	738(61)	740(vs)	C-Cl stretching
792(42)	800(61)	800(vw)	C-F i p bending
805(70)			C-H o p bending
833(14)		826(vw)	C-H o p bending
855(70)	851(68)		C-H o p bending
	881(34)	880(w)	C-H o p bending
890(90)	900(79)	900(vs)	C-C stretching (ring breathing)
922(30)	942(16)		C-H o p bending
	991 (34)	995(vw)	C-C-C i.p. def.
1037(15)	1034(82)	1040(w)	CH_3 rocking
1075(100)	1070(11)		CH rocking
1123(52)	1122(20)	1120(w)	C-H i.p bending
1187(62)	1175(63)	1178(w)	C-F stretching
1225(80)	1234(85)	1235(vs)	CH_3 stetching
1266(62)	1258(67)	1259(w)	C-H i p. bending
1290(40)	1278(25)	1280(vw)	C-H i p bending
	1377(35)	1379(m)	C-C stretching
1381(30)	1391(26)		C-H sym def in CH_3
	1434(36)	1439(w)	C-H asym. def. in CH_3
1445(35)	1450(38)	1448(w)	C-H asym def. in CH_3
	1459(29)		C-H asym. def in CH_3
1490(100)	1486(100)	1485(vw)	C-C stretching
	1507(26)		C-C stretching
1587(80)	1578(54)	1581(w)	C-C stretching
1613(60)	1604(78)	1603(w)	C-C stretching
2865(16)	2866(20)	2866(w)	C-H sym stret. in CH_3
2930(27)	2925(30)	2925(ms)	C-H asym stret in CH_3
2960(20)	2966(25)	2965(vw)	C-H asym stret. in CH_3
3037(15)	3034(20)	3042(vw)	C-H stretching
3037(16)	3081(23)	3076(ms)	C-H stretching

Note : The intensity is given in the parenthesis.

i p = in plane, o p = out of plane; sym = symmetrical; asym = assymmetrical, def = deformation, stret = stretching, s = strong; ms = medium strong; m = medium, w = weak and vw = very weak.

The liquid sample of 4-fluoro-2-chlorotoluene was obtained from Koch-Light Laboratories, U K. and was used as such The infrared spectrum was recorded on a Perkin Elmer Grating Spectrophotometer model 621 in the range 300-4000 cm $^{-1}$ on high resolution The Raman spectrum was recorded on Codec using argon ion laser The vibrational frequencies and their proposed assignments alongwith relative intensities are given in table 1 The vibrational frequencies of 2-fluoro-4-chlorotoluene is also included for the comparative study

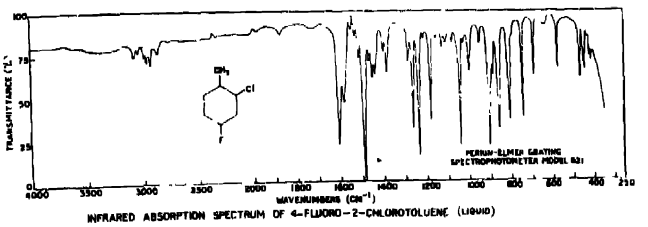

Fig 1

The molecule 4-fluoro-2-chlorotoluene may be classified into C_s point group if the CH_3 group is considered as a point mass The 30 benzene like modes can be divided as 21a′ (planar) and 9a″ (non-planar) vibrations In addition to these vibrations a few more vibrations will be present due to the internal vibrations of methyl group

The assignments of the observed bands have been made on the basis of their intensities and postions in the spectrum and the vibrational assignments reported for similar molecules such as toluene, chlorotoluene, fluorotoluene and 2-fluoro-4-chlorotoluene. Most of the observed bands have the same trend as already reported in the case of 2-fluoro-4-chlorotoluene But there are a few differences which are as follows The C-C stretching mode arising from 1485 cm $^{-1}$ of benzene split up into two components in the molecules of C_s symmetry The band observed at 1507 and 1486 cm $^{-1}$ are assigned to this mode But only one band at 1490 cm $^{-1}$ is reported by Joshi & Sharma (1974) for this mode in the spectrum of 2-fluoro-4-chlorotoluene

The C-F stretching and C-CH_3 stretching modes arise in the same region of the spectrum and it becomes generally difficult to assign properly in this situation But when the masses of fluorine atom and the methylgroup are taken into account for the simplicity, one may guess to some extent that the C-F stretching mode appears lower than C-CH_3 stretching mode in magnitude. Under this simple assumption the band observed at 1175 cm^{-1} and 1234 cm $^{-1}$ have been assigned to C-F and C-CH_3 stretching modes respectively

The 1210 cm^{-1} mode of benzene is substituent sensitive and its magnitude generally varies to a great extent. The band observed at 1377 cm^{-1} is identified to this mode in the present case,

A few bands observed are assigned to combination and overtone bands but they are not included in the table

The thermodynamic functions i.e heat capacity (C_v^0), enthalpy function ($H^0-E_0^0/T$), free energy ($G^0-E_0^0/T$) and entropy (S^0) of 2-fluoro-4-chlorotoluene and 4-fluoro-2-chlorotoluene molecules have been calculated utilising the observed

Table 2

Moments of inertia	2-Fluoro-4-Chlorotoluene	4-Fluoro-2 Chlorotoluene
I_x	1257	1225
I_y	950	683
I_z	307	542

Table 3. Thermodynamic functions (in cal/mole/°K)

2-fluoro-4-chlorotoluene

°K	C_v^0	$\frac{(H^0-E_0^0)}{T}$	$-\frac{(G^0-E_0^0)}{T}$	S^0
100	7.0	8.0	51.8	60 0
200	12.3	9 8	57.2	67.0
298 16	19.1	12 5	62 3	74 8
300	19.2	12 5	62 3	74 8
400	26.2	15.5	66 3	81.8
500	32 0	18.6	70.1	88 7
600	36.3	21 6	73 9	95 6
700	39.5	24.1	77.3	01.4
800	42 2	26.5	80 7	107.2
900	43 2	28.6	83.9	112.5
1000	45.7	30.5	87.1	117.6
1100	47.0	32.1	90.0	122 1
1200	47.9	33.5	92.9	126.4
1300	48.7	34.9	95 7	130.6
1400	49.3	36.0	98.5	134.5
1500	49.8	37.0	100.0	137,8

Table 3(Contd)

4-fluoro-2-chlorotoluene

°K	C_p^0	$\frac{(H^0-E_0^0)}{T}$	$-\frac{(G^0-E_0^0)}{T}$	S^0
100	6.5	8.0	52 0	60 0
200	11 1	9.2	57 1	66 3
298 16	18 3	11 6	61 9	73 5
300	18.5	11 7	62.0	73 7
400	26 4	14.9	65.8	80 7
500	33.4	18 3	69 5	87 8
600	38.9	21 7	73 1	94 8
700	43.3	24 7	76 7	101 4
800	46 6	27 6	80 3	1p7 9
900	49 2	30 0	83 6	113 6
1000	51 2	32.2	86 9	119 1
1100	52 8	34 2	90.1	124 3
1200	54 0	36 0	93.1	129 1
1300	55 0	37.6	96.1	133.7
1400	55.9	39 0	98 9	137 9
1500	56 5	40.2	101 6	141 8

vibrational data. The structural data have been taken from the similar molecules *i e* C—C = 1 4Å, C—H = 1.08Å, C—CH_3 = 1.69Å, C—F = 1.39Å, C—Cl = 1 69Å and all angles are 120°. The moments of inertia I_x, I_y and I_z along the axes X, Y and Z have been calculated where Y and Z are in the plane and X axis is perpendicular The value of symmetry parameter element α is determined from the symmetry element and is 1 for C_s symmetry. The values of moments of inertia and the thermodynic functions are given in tables 2 and 3 respectively.

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